GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 1/19/81

Project Title: Hydrogenation vs. Hydrogenolysis Selectivity of Bimettallic Catalysts During Reduction of Low Molecular Weight Nitriles

Project No: E-19-638

Project Director: Dr. P.K. Agrawal

Sponsor: Dow Chemical Company; Midland, Michigan 48640

Agreement Period: From 2/1/81 Until 1/31/82 (Perf. & Rpts.)

Type Agreement: Standard Industrial Agreement dated 12/9/80

Amount: $17,856
$10,726 GIT (E-19-355)
$28,582

Reports Required: Quarterly Letter Progress Reports

Sponsor Contact Person (s):

Technical Matters

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Midland, Michigan 48640
517/636-1404

Contractual Matters
(thru OCA)

Michael L. Glenn
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Defense Priority Rating: None

Assigned to: Chemical Engineering (School/[illegible])

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Other: OCA Research Property Coordinator
Project Code (OCA)

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

2R464 2

Date 7/12/82

Project Title: Hydrogenation vs. Hydrogenolysis

Project No: E-19-638

Project Director: Agrawal

Sponsor: Dow Chemical Co.

Effective Termination Date: 1/31/82

Clearance of Accounting Charges: _____

Grant/Contract Closeout Actions Remaining:

- [x] Final Invoice ~~and Closing Documents~~
- [ ] Final Fiscal Report
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Assigned to: ChE (School/Laboratory)

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FORM OCA 10:781

E-79-638

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

May 5, 1981

Dr. C. E. Wymore
Central Research
1776 Building
Chemical Process Laboratory
Dow Chemical Company
Midland, Michigan 48640

Dear Dr. Wymore:

This is to bring you up to date on the current status of the research project entitled "Hydrogenation vs Hydrogenolysis Selectivity of Bimetallic Catalysts during Reduction of low Molecular Weight Nitriles".

The first part of this research project involves the design, construction and testing of the atmospheric pressure reactor. Figure 1 shows a schematic of the experimental reactor. The reaction will be conducted in the gas phase, so it will be necessary to maintain temperatures in excess of 150°C to prevent any condensation of nitrile reactants and/or its derivatives. Butyronitrile will be introduced into the reactor system through a Sage® syringe pump; constant pumping speeds over a period of 20 hr can be achieved. The sharp end of the stainless steel syringe needle will be welded into a 1/8" SS tubing which is heated externally using heating tapes. This will cause the nitrile reactant to evaporate before mixing with H_2. The reactant mixture (nitrile + H_2) then enters the quartz tube reactor through a Tee connection the other end of which is to be employed for measuring the catalyst bed temperature. A digital temperature readout (model no. 199, Omega Engineering) will be used to record the temperature using a chromel-alumel thermocouple embedded in the catalyst bed. The quartz tube (6mm O.D.) will be heated externally by using ceramic heating blocks. A thermocouple in between the reactor tube and the heating block will be used as a sensor for temperature control. Honeywell temperature controller (model # AV-726 HB114) will supply the power to the heating blocks. This mode of temperature sensor and power supply provides a closer temperature control (with in $\pm$ 1°C) without much oscillations.

Thermal conductivity detector in gas chromotograph (Hewlett-Packard) model no 5730) will be used to analyze the reactor effluent. Due to lack of experimental documentation, it is proposed that two column packing materials be tried and then choose the better one. The first one is carbopak B/4% carbowax 26 m/0.8% KOH, and the second one is 10% carbowax 20M-2% KOH on 80/100 chromosorb W/AW, both to be supplied by Suppleco. The primary objective is to separate nitrile and amines whereas the secondary objective is to separate the amines themselves. It may become necessary to use two columns to achieve effective separation.

There is yet another aspect which needs to be resolved, i.e. adequate method of removing the nitriles and its derivatives (primarily amines) from the reactor effluent before venting H_2 into the exhaust hard. It is speculated that passing the GC effluent gas through some organic solvent should resolve that problem. However, no effort as yet has been directed towards that goal.

At present, all the major components for reactor construction have been purchased, and the construction will start soon. At the same time, order has been placed for the above-mentioned column packing materials. While the reactor is being constructed, efforts will be made to develop analytical procedures and standards in gas chromatography.

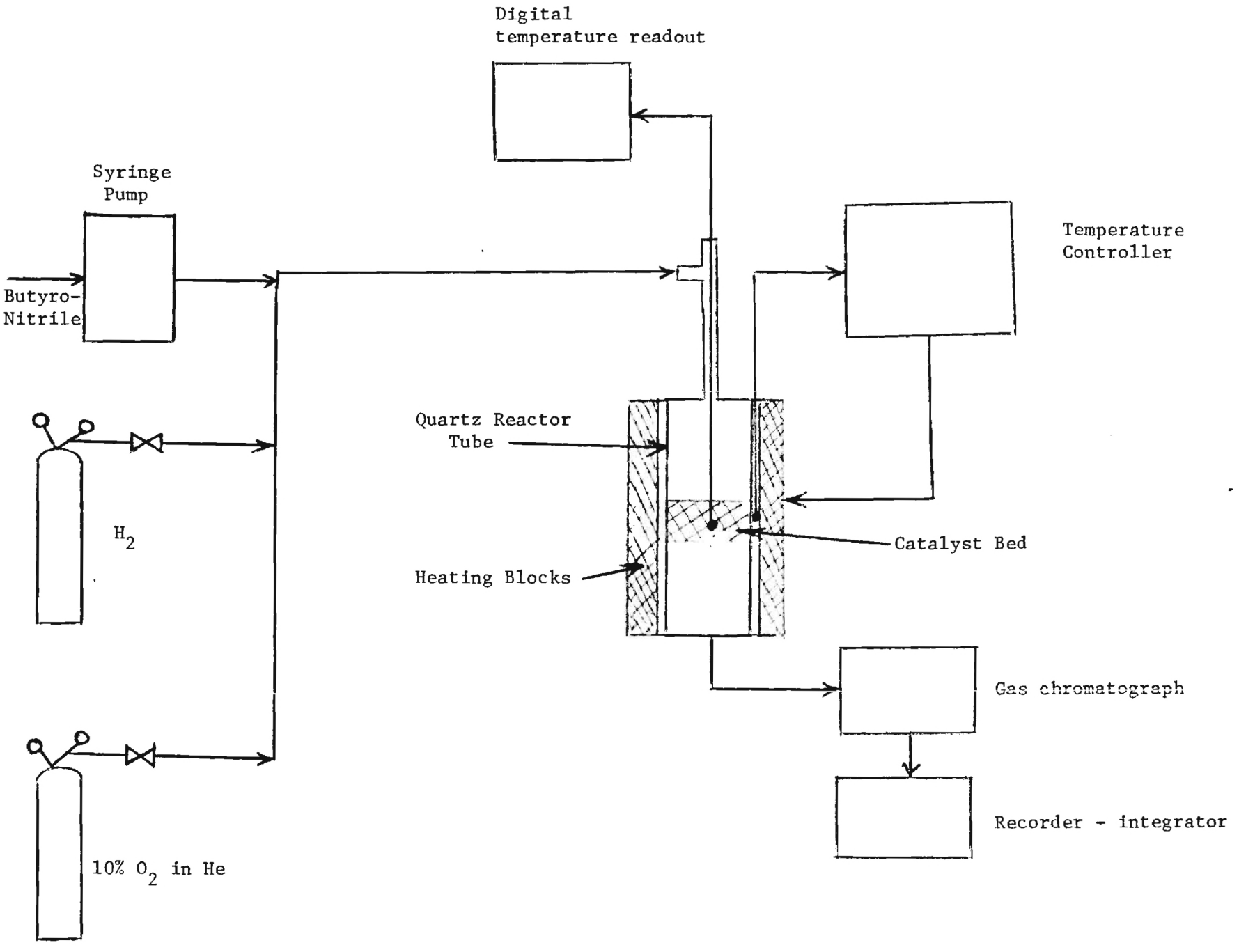
Please let me know if you have any questions or suggestions. Please call me at (404) - 894-2826.

Best regards.

Sincerely,

Pradeep K. Agrawal
Assistant Professor

PKA/llc



A Schematic of the Flow Reactor

E-19-638

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

August 5, 1981

Dr. Edward Vrieland
Central Research
1776 Building
Chemical Process Laboratory
Dow Chemical Company
Midland, Michigan 48640

Dear Dr. Vrieland:

This is the second quarterly progress report on the project entitled, "Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts during Reduction of Low Molecular Weight Nitriles," covering the period 5/1/81 to 7/31/81. Since we have already discussed the project at length on 7/17/81, this report will provide only a brief summary of our activities during the past three months.

Mr. You Sung Won, who joined our graduate program in Summer Quarter (beginning June 15, 1981), is working on this project. Mr. Won has a B.S. and M.S. degree in Chemical Engineering from the Hanyang University in Seoul, South Korea. He has experience in working with the reactor systems. During the past six weeks, Mr. Won has already studied the pertinent literature dealing with the reaction and catalyst system and has located 3 or 4 useful papers which confirm our earlier choice of column packing material (carbopak B/4% carbowax 26 m/0.8% KOH and 10% carbowax 20 m-2% KOH on 80/100 chromosorb w/aw) to be the right one. He has prepared columns of each packing and is ready to test them in the gas chromatograph.

All but two components (temperature controller and heating furnace) have been received and the remaining two components are expected to arrive within a week or two. The experimental layout, reactor platform and other components of the reactor system have already been constructed. It is expected that the reactor will be operational by 9/15/81. By that time, we also expect to have the GC operation (including calibration) ready. So, it appears that our preliminary catalyst testing will begin in September, 1981 and within a month after that we will be testing bimetallic catalysts.

In the preparation of bimetallic catalysts, we have decided to focus on Pt-Au alloy system rather than Pt-Ag alloy system. There is evidence from the work of Professor Somorjai (University of California, Berkeley) that Au is statistically distributed on the Pt surface whereas Ag is preferentially

present on the terrace-sites of Pt. So, we expect Au to be better than Ag in improving the selectivity.

Please call me at 404-894-2826 if you have any questions, comments or suggestions.

Best regards.

Sincerely,

Pradeep K. Agrawal
Assistant Professor

PKA/sm

cc: Dr. C. E. Wymore

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

November 6, 1981

Dr. Edward Vrieland
Central Research
1776 Building
Chemical Process Laboratory
Dow Chemical Company
Midland, Michigan 48640

Dear Ed:

Please find enclosed the third quarterly progress report on the project entitled, "Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts during Reduction of Low Molecular Weight Nitriles," covering the period 8/1/81 to 10/31/81. Much has happened since our last progress report. Mr. Won who had joined us to work on this project in June, 1981 left U.S.A. to return to S. Korea in August, 1981 for personal reasons. Mr. William Seely, a junior in our undergraduate program, started to work on this project as soon as Mr. Won left the project. Bill worked on an hourly-wage basis in the capacity of a research assistant. His first task was to identify the appropriate column for separating the products and to find the optimum column operating conditions. It is found that the packing "carbopak B/4% cw 20M/0.8% KOH" on a 1/4", 6 ft long glass column is a good one in separating the reactants from the amine products. Also all the three amine products can be separated under the same conditions. The column is temperature-programmed from 160°C to 210°C at a rate of 8°C/min. The second task which Bill undertook was to assemble the reactor components and to do a test run. This resulted in only a partial success. The pressure drop through the reactor was too large. As a result the H_2 gas diffused into the syringe pump which caused the nitrile concentration to widely vary in the feed stream.

Since September 15, 1981, Mr. Scott McMillan has joined this project. Scott received his B.S. in Chemical Engineering from the U. of Delaware in June, 1981. He worked with Professor J. R. Katzer on his B.S. thesis in the area of CO hydrogenation reactions. I am sending a copy of his B.S. thesis to you under a separate cover as per our earlier conversation.

Most of the work described below is the result of Scott's efforts during the past six weeks, despite his carrying a full-time graduate course load. He has received occasional assistance from Bill Seely in this work. Figure 1 shows the calibration of TC detector using known mixtures of butyronitrile, butyl amine, and dibutyl amine. A linear response of each component (in concentrations upto 3200 ppm (by volume)) is observed. Figure 2 shows the modified reactor flow diagram. The original design of reactor tube resulted in a very large pressure drop across the reactor bed. This caused substantial backflow of H_2 into the syringe pump. Use of check valves has practically removed this problem. The diameter of the catalyst bed has also been doubled to reduce the catalyst packing height, and this has resulted in a complete elimination of H_2 backflow. Also shown in Fig. 2 is a gas manifold system, which enables H_2 reduction of catalyst, oxygen treatment of deactivated catalyst, and flushing cycle of He in between. A reactor bypass line has been added to permit direct injection of feed mixture into the gas chromatograph.

Out of 3 or 4 test runs, one successful run has been made using this flow system. A 0.1 gm of 1% Pt/Al_2O_3 catalyst was charged into the reactor. Feed mixture consisted of 48% butyronitrile and 52% H_2. At 1 atm, and at 250°C the effluent stream contained 36% nitrile, 43% H_2, 10% butyl amine and 11% dibutylamine. The reaction rate for butylamine formation is computed to be 0.0582 gmoles/gcat-sec under these reaction conditions. Figure 3 shows the histogram of the inlet and outlet streams; steady-state was reached after 3.5 hr of operation. Figure 4 shows a typical chromatogram under these reaction conditions. Apparently, high selectivity towards the formation a dibutylamine may have been the result of a very high nitrile/hydrogen molar ratio in the feed stream.

At this point, we are still trying to identify the reaction conditions under which measurable quantities of hydrocarbons are formed. Only then shall we proceed towards the use of bimetallic catalysts. Next week, after you have had a chance to go through this report, I shall contact you to discuss these results and the direction in which we plan to move.

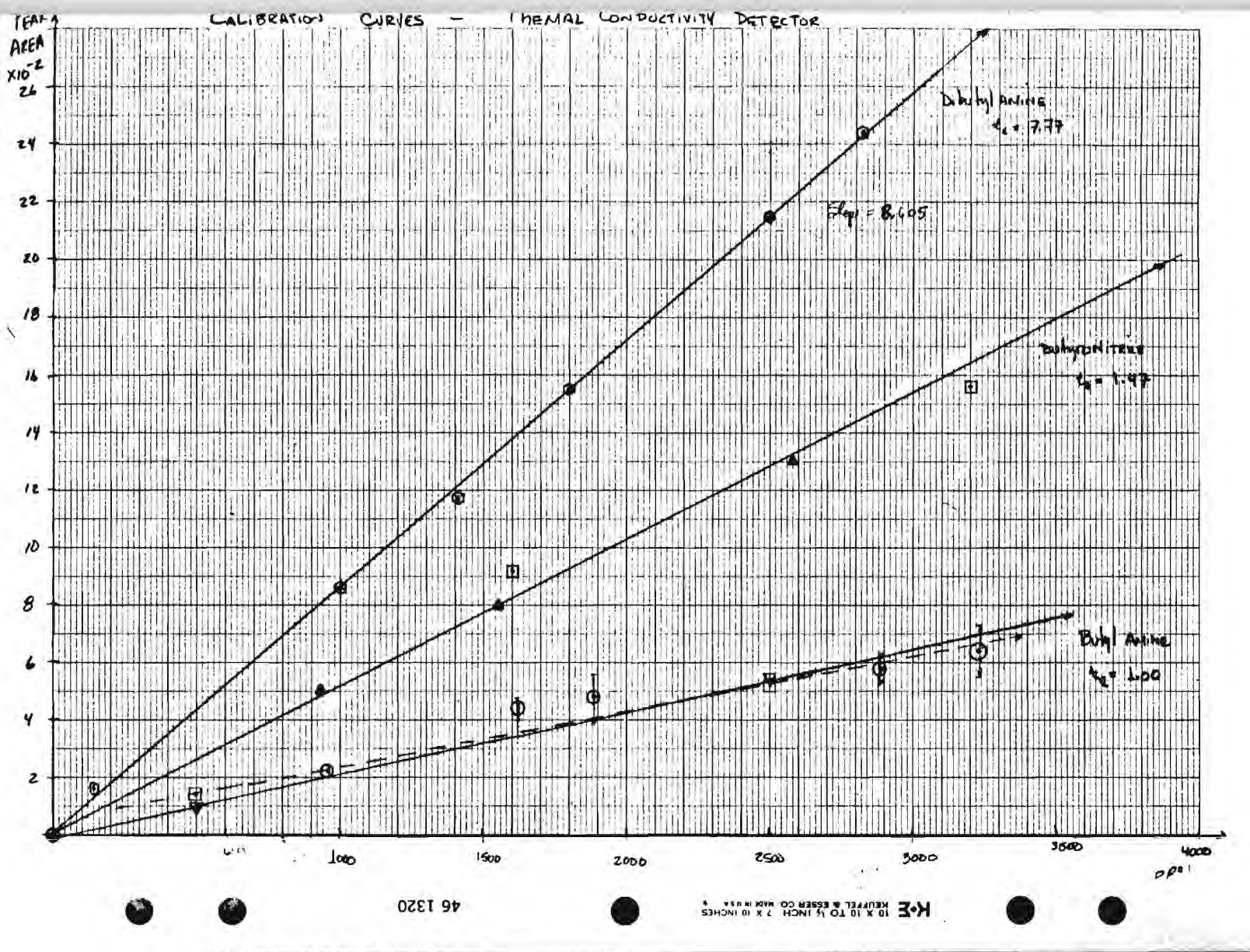
With best regards.

Yours sincerely,

Pradeep.

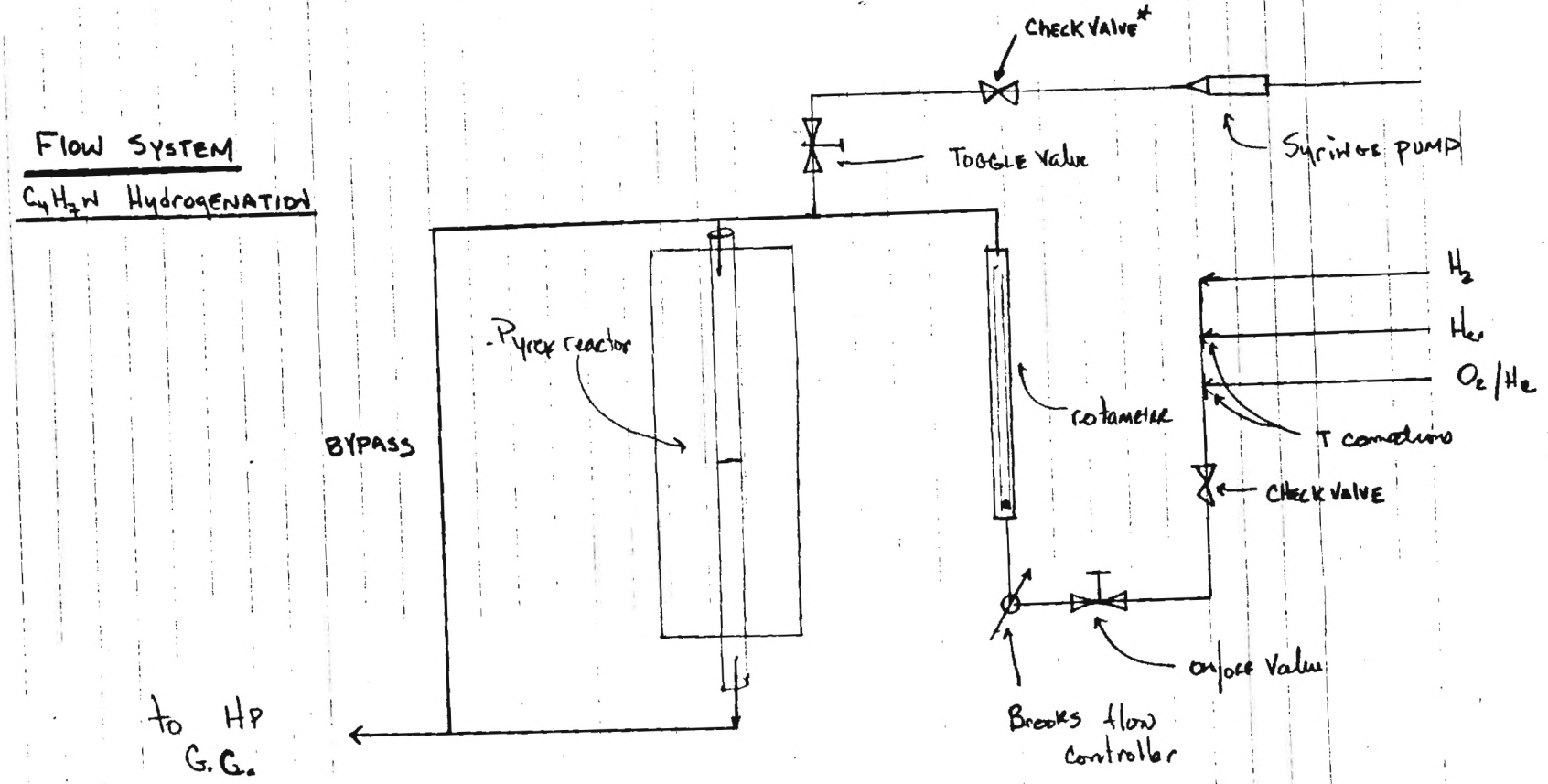
Pradeep K. Agrawal
Assistant Professor

PKA/sm
Enclosure

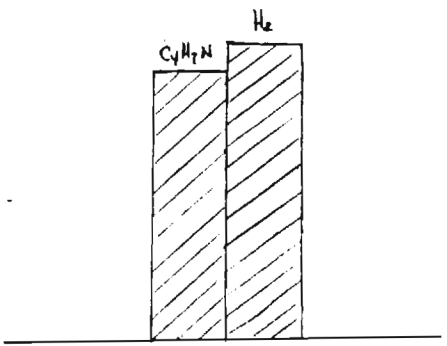

CALIBRATION CURVES — THEMAL CONDUCTIVITY DETECTOR
PEAK AREA X10⁻²
Dibutyl Amine
t_R = 7.77
Slope = 8.405
Butylbenzene
t_R = 1.97
Butyl Amine
t_R = 1.00
26
24
22
20
18
16
14
12
10
8
6
4
2
1000
1500
2000
2500
3000
3500
4000
46 1320
K+E
10 X 10 TO ½ INCH 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

Flow System

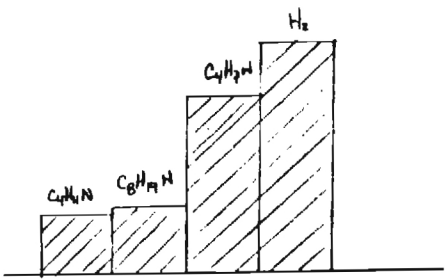
C_4H_2W Hydrogenation



HISTOGRAM RUN #1 0.1% Pt/Al_2O_3

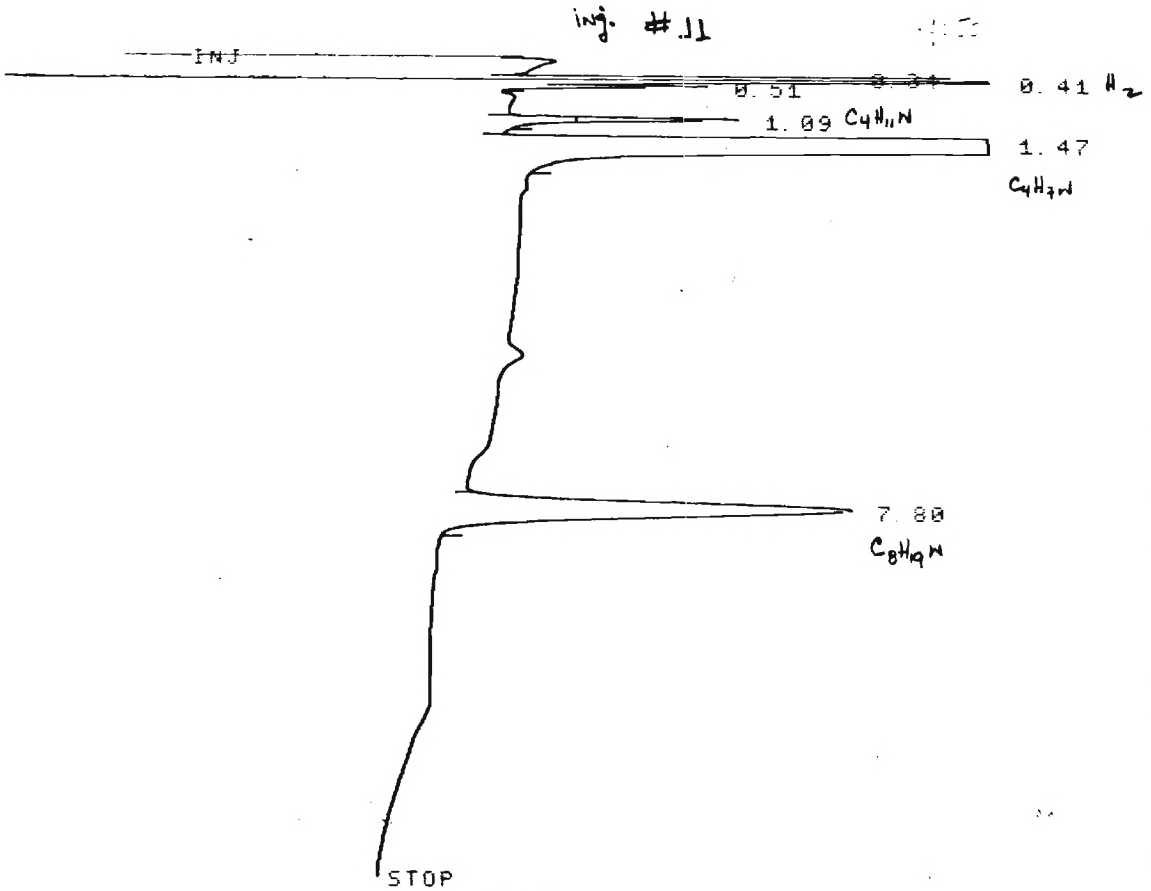


REACTOR INLET



REACTOR OUTLET

HP 3380A
DLY OFF STOP OFF REJECT OFF
MV/M .30 ATTN 1



Sample Chromatogram Run #1 0.1% Pt/Al_2O_3

AREA %

RT	TYPE	AREA	
.34		2354	.943 6
.41	M	9354	3.75
.51	M	3783	1.516
1.09		1248	.500 3
1.47		224911	90.16
7.80		7819	3.134

HP 3380A
DLY OFF STOP OFF REJECT OFF
MV/M .30 ATTN 1

INJ

E-19-638

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

February 5, 1982

Dr. Edwin Vrieland
Central Research, 1776 Building
Chemical Process Laboratory
Dow Chemical Company
Midland, Michigan 48640

Dear Ed:

It was a pleasure to have you visit us earlier this week on February 1, 1982. Although we discussed during your visit our progress on the project entitled "Hydrogenation vs. Hydrogenolysis selectivity of Bimetallic Catalysts during Reduction of Low Molecular Weight Nitriles" at some length, this letter is to provide a formal fourth quarterly progress report for the period 11/1/81 - 1/31/82.

In the previous report we had stated the results obtained on 1% Pt/Al_2O_3 catalyst. Since then we have tried to prepare our own Pt/Al_2O_3 catalyst in the laboratory. The catalyst preparation method is as follows: approximately 2 gm of γ-Al_2O_3 is impregnated with the aqueous solution of chloroplatinic acid; enough platinum is present in the aqueous solution to give 1 wt% Pt on Al_2O_3. The volume of aqueous solution is just enough to fill the void pores of porous alumina powder. The impregnating solution is added slowly to alumina in a crucible while stirring it gently. The wet cake thus obtained is not filtered as there is no excess solution. The cake is dried in stagnant air at 100°C and then calcined in flowing O_2/He (50 cc/min) at 350°C for 3 - 4 hours. The catalyst obtained is loaded into the reactor and reduced at 350°C with H_2 flowing at 50 cc/min for 16 hours. After reduction, the temperature is lowered to the desired reaction temperature, and the reaction is started by feeding the reactant mixture.

The reaction studies on the catalysts prepared by the above method show that the extent of cracking is greater than that observed on the previous Pt/Al_2O_3 catalysts (acquired from the laboratory of Dr. W. R. Ernst). Earlier progress report (dated 11/6/81) indicated the results obtained on 1% Pt/Al_2O_3 (Dr. W. R. Ernst). Using catalysts prepared in our laboratory, we observe about equal amounts of butyl amine and dibutyl amine, a significant amount of butane, traces of propane, and ammonia at 250°C when 10% butyronitrile (balance H_2) is fed to the reactor. When the reaction temperature was reduced to 180°C, no butyl amine was observed; traces of dibutyl amine are observed. The major reaction product now is butane. An increase of temperature to 205°C results in significant amounts of dibutyl amine, but still no butyl amine is observed. Also, the amount of butane increases. The amount of tributyl amine product remains negligibly small at all three temperatures.

Undoubtedly, the source of butane appears to be butyl amine but propane can be obtained by one of the following two reactions:

$$CH_3-CH_2-CH_2-CN + H_2 \longrightarrow CH_3-CH_2-CH_3 + HCN \quad (1)$$

$$CH_3-CH_2-CH_2-CH_2-NH_2 + H_2 \longrightarrow CH_3-CH_2-CH_3 + CH_3-NH_2 \quad (2)$$

The primary source of trace propane quantities appears to be the first reaction since no traces of methyl amine were observed. In the event of either reaction, some C-C bond cracking is being observed. However, the extent of C-C cracking is significantly smaller than the extent of C-N cracking. We have been successful in separating the propane and butane from H_2 on the same column (carbopak B/4% carbowax 20 M/0·8% KOH) at room temperature. Presently attempts are being made to calibrate the GC for these lighter cracking products.

Another point which we discussed during your visit was the possibility of chlorine being present on alumina, specifically because of the extent of cracking reaction. It is very likely that the chlorine present during impregnation may not have been removed because of low-termperature reduction (350°C). A reduction temperature of 500°C appears to be more suitable for chlorine removal, and we will try that in our next run. Meanwhile, if the above treatment does not affect the reaction products significantly, we will try to treat the impregnated catalyst with aqueous solution of KOH at 60 - 80°C to reduce the acidity of support. I am looking forward to receiving a sample of Pt/Al_2O_3 catalyst from your laboratory. I believe that these above series of treatments will point the right direction for preparing a reproducible Pt/Al_2O_3 catalyst. I am also proposing to study if any cracking occurs on the support itself. We will try to study that by feeding butyronitrile, and butylamine with H_2 over Al_2O_3 powder alone at the reaction temperatures.

I will keep you posted on the results obtained during our studies. Please call me at (404) 894-2826 if you have any suggestions or comments.

With best regards.

Yours sincerely,

Pradeep K. Agrawal
Assistant Professor

PKA:law